Basic Thermodynamics

First Law of Thermodynamics

Basically a statement of conservation of energy which includes heat as a form of energy:

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W,$$

where $\mathrm{d}Q$ is **heat absorbed** by the system, and $\mathrm{d}W$ is **work done on** the system. U is a function of state called **internal energy**.

Zeroth Law of Thermodynamics

Suppose A, B and C are distinct thermodynamic systems. If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then A is in thermal equilibrium with C.

Systems in thermodynamic equilibrium can be described in terms of physical variables that do not change with time. The Zeroth Law implies that there exists some physical property which systems that are in thermal equilibrium have in common, regardless of their size, shape, substance, etc. We call this property **temperature**. A **thermometer** is a device that can be used to assign a numerical value to temperature through measurements of a physical property.

Constant-volume gas thermometer. The mercury reservoir is raised or lowered to adjust the difference in height h between the two mercury columns M and M' so that the volume of gas in the bulb + capillary is constant.

Absolute temperature (perfect gas scale)

$$T(\mathrm{K}) = 273.16 \frac{\lim_{p \to 0}(pV)_T}{\lim_{p \to 0}(pV)_{\mathrm{TP}}},$$

where TP stands for the triple point of water.
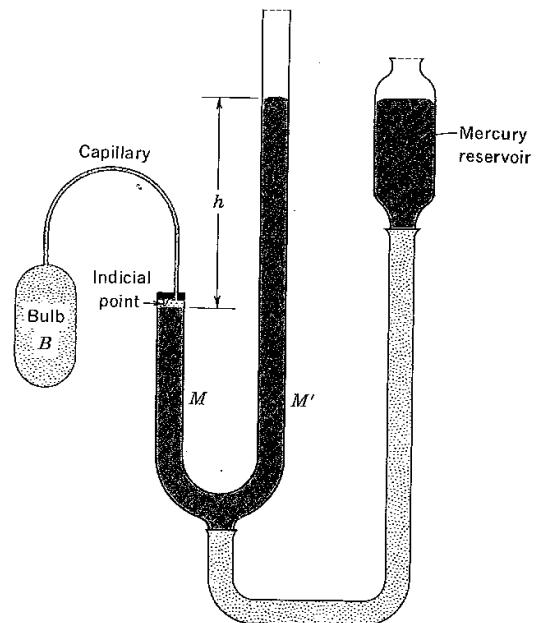
Right: Readings of a constant-volume gas thermometer for the temperature of condensing steam as a function of the pressure p_3 at the triple point of water. Curves for different gases are shown. The readings extrapolate to the same value θ(steam) at low pressure, independent of the gas.
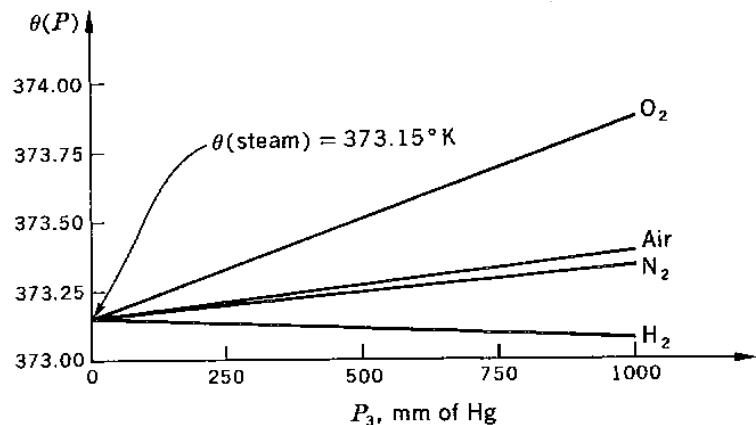
Exact differentials

In multivariate calculus, an expression such as $F_1(x, y)\,\mathrm{d}x + F_2(x, y)\,\mathrm{d}y$ is known as an **exact differential** if it can be written as the differential

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y,$$

of a differentiable single-valued function $f(x, y)$. This implies that

$$F_1 = \left(\frac{\partial f}{\partial x}\right)_y \qquad F_2 = \left(\frac{\partial f}{\partial y}\right)_x,$$

or in vector form $\mathbf{F} = \nabla f$. Hence the integral of an exact differential is path-independent so that [where 1 and 2 are shorthands for (x_1, y_1) and (x_2, y_2)]

$$\int_1^2 F_1(x, y)\,\mathrm{d}x + F_2(x, y)\,\mathrm{d}y = \int_1^2 \mathbf{F} \cdot \mathrm{d}\mathbf{r} = \int_1^2 \mathrm{d}f = f(2) - f(1),$$

and the answer depends only on the initial and final states of the system. For an **inexact differential** this is not true, and knowledge of the initial and final states is not sufficient to evaluate the integral: you have to know which path was taken.

For an exact differential the integral round a closed loop is zero:

$$\oint F_1(x, y)\,\mathrm{d}x + F_2(x, y)\,\mathrm{d}y = \oint \mathbf{F} \cdot \mathrm{d}\mathbf{r} = \oint \mathrm{d}f = 0,$$

which implies $\nabla \times \mathbf{F} = 0$ (by Stokes' theorem) and hence

$$\left(\frac{\partial F_2}{\partial x}\right)_y = \left(\frac{\partial F_1}{\partial y}\right)_x \qquad \text{or} \qquad \left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right).$$

Functions of state have exact differentials with respect to each other.

Heat capacity

Suppose an amount of heat ΔQ is transferred to a system while the variable x is held constant, and as a result the temperature of the system changes by ΔT. We define the *heat capacity at constant x* by

$$\begin{aligned} C_x &= \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}\bigg|_x \\ &= \left(\frac{\partial Q}{\partial T}\right)_x \end{aligned}$$

Heat capacities are commonly measured at constant volume (C_V) or at constant pressure (C_p).

The **specific heat capacity** is the heat capacity per unit mass. It is usually written in lower case: $c_x = C_x/m$. The **molar heat capacity** is the heat capacity of one mole of substance.

For a system in which $\mathrm{d}W = -p\mathrm{d}V$, such as a gas,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

For one mole of an *ideal gas*, $C_p = C_V + R$, where $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$ is the gas constant.